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AEROGEL AND ADHESIVE-CONTAINING COMPOSITE, PROCESS FOR ITS
PRODUCTION AND ITS USE

Inventors; and
(only for U.S.):

Fritz Schwertfeger [DE/DE]
Rauenthaler Weg 32,
D-60529 Frankfurt am Main (DE)

Andreas Zimmermann [DE/DE]
Im Dürren Kopf 27a
D-64347 Greisheim (DE)

Johann Wonner [DE/DE]
Konstanzer Straße 64,
D-60386 Frankfurt am Main (DE)

Frank Scholl [DE/DE],
Industriestraße 2F
D-63543 Neuberg (DE)
Marc Schmidt [DE/DE]
Rauenthaler Weg 33
D-60529 Frankfurt am Main (DE)

Applicant (for all
designated states
except the U.S.A.:

Hoechst Aktiengesellschaft [DE/DE]
Brüningstraße 50
D-65929 Frankfurt am Main (DE)

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The patent pertains to a novel composite material of arbitrary form with high thermal insulation capacity, containing from 5-97 vol% aerogel particles and at least one adhesive, the particle diameter being less than 0.5 mm.

Conventional insulation materials based on polystyrene, polyolefins and polyurethanes are produced, as a rule, using organic propellants, such as chlorofluorocarbons (CFCs). The propellant contained in the cells of the foam material is responsible for the high thermal insulation capacity. Such propellants pollute the environment, since they slowly escape into the atmosphere.

Also known are molded articles that contain thermoplastic resins such as urea, melamine and phenol formaldehyde resins, or mixtures of these resins. These resins are mixed with fillers such as sawdust, asbestos and especially cellulose, possibly also with lubricants such as zinc stearate, pigments such as titanium dioxide, plasticizers such as glycerin and/or o, p-toluenesulfonamides and/or acidic or acid-hydrolyzing curing accelerators into so-called molding compositions that are cured in molds under application of pressures of 100-2500 bar and temperatures of 100-200°C into molded articles (Plastics Handbook 10 "Thermosetting materials," ed. Prof. Woebcken, 2nd ed. 1988, Hanser Verlag, pp. 266-274). These resins can be used as powdered resins in the so-called complete fusion method or as liquid resins in the liquid resin method. The composition of a typical molding composition according to DIN 7708 Type 152 looks as follows:

- 50 wt% melamine formaldehyde resin

- 35 wt% bleached sulfite cellulose

- 1 wt% lubricants, e.g. zinc stearate

- 10 wt% white pigment, e.g. lithopone

- 1 wt% curing accelerator and

- 3 wt% plasticizer

Such standard test specimens obtained according to DIN 7708 have densities 1.5-2.0 g/cm³ and thermal conductivities of 300-600 mW/m·K (Plastics Handbook 10 "Thermosetting Materials," ed. Prof. Woebcken, 2nd ed. 1988, Hanser Verlag, pp. 269-270). They are therefore not suited for use in thermal insulation.

Aerogels, especially those with porosities over 60% and densities under 0.6 g/cm^3 have a very low thermal conductivity due to their very low density and high porosity and thus find application as thermal insulation materials, as, for instance, in EP-A-0171 722.

The high porosity, however, also causes low mechanical stability, of both the gel from which the aerogel is dried out and of the dried gel itself.

It is likewise known that aerogels have extraordinarily low dielectric constants with values of 1-2, depending on the density of the aerogels. Aerogels are therefore ideal for electronic applications, such as high-frequency applications (see C.W. Hrubesch et al., J. Mater. Res., Vol. 8, No. 7, 1736-1741).

Aerogels in the broader sense, i.e. in the sense of "gel with air as dispersion means," are produced by drying a suitable gel. The term "aerogels" in this sense includes aerogels in the narrower sense, xerogels, and cryogels. A dried gel is designated an aerogel in the narrower sense if the fluid of the gel is removed at temperatures above the critical temperature and starting from pressures above the critical pressure. If, on the other hand, the fluid is removed subcritically, while forming a liquid-vapor boundary phase, for instance, then the resultant gel is often referred to as a xerogel. It should be noted that the gels according to the invention are aerogels in the sense of being a gel with air as the dispersion means.

The process of forming the aerogel is finished during the sol-gel transition. After forming the solid gel structure, the external form can be changed only by comminution, grinding for instance.

For many applications, it is necessary, however, to utilize the aerogels in definite forms. For this purpose, it is necessary to conduct a forming step following the aerogel production, that is, after drying, without any substantial change of the internal structure of the aerogel occurring with regard to the application.

In EP-A-0 340 707 an insulation material with a density of $0.1\text{-}0.4 \text{ g/cm}^3$ is disclosed, consisting of at least 50 vol% silica aerogel particles with a diameters of 0.5-5 mm, which are joined together by means of at least one organic and/or inorganic binder.

Disclosed as organic binders here are reaction adhesives, silicon resin adhesives, hot-melt adhesives and aqueous dispersion adhesives.

The relatively coarse grain structure has the effect, however, that the manufactured insulation materials have no uniform appearance, which is disadvantageous for many applications. The relatively coarse grain structure also has the effect that molded articles produced from the insulation materials have a nonhomogeneous distribution of the aerogel material. This is particularly true if the smallest typical dimensions of the molded articles, namely the thickness in the case of films or mats, is not much larger than the typical aerogel particle diameter. A higher binder content would be needed, particularly in the edge areas, which

would then have a negative effect on the thermal conductivity and the dielectric properties of the molded article, especially at the surface.

Particularly in electronic applications, thin films (0.01-2.0 mm) are needed, which cannot be produced from the above-described aerogel particles.

In a molded article made from this insulation material, moreover, areas of low mechanical stability made of aerogel materials with diameters of 0.5-5 mm, would arise, which could result, under mechanical stress, in surface unevennesses with diameters or depths of up to 5 mm, due to destruction of the aerogels at the surface.

Due to the coarse grain structure of the aerogel it is also not possible to produce film-like thermal insulation elements with a thickness of less than 0.5 mm. Even thicker film layers suffer, however, from the relatively large aerogel particles in relation to the film thickness, since an elevated binder content is required, particularly in the edge areas, which would then have a negative effect on the thermal conductivity and the electronic properties of the dried film or the dried molded article.

Furthermore, a process is described in EP-A-0 340 707, according to which the aerogel particles are coated and/or mixed with a binder and the mass obtained is subsequently cured in a mold. Due to the great difference in density between the aerogel and the inorganic and/or organic binder and the size of the aerogel particles, the mixed mass tends to be demixed, that is, it is unstable over the relatively long time required for utilization and storage. Consequently the shaping can be done only by relatively fast curing of the mixed mass in a surrounding mold.

It is additionally not simple to produce such insulation materials with only a low liquid content, since with the process specified in EP-A-0 340 707 the aerogel particles can easily be destroyed by shearing processes during mixing due to their low mechanical strength.

The problem is therefore to prepare an aerogel-based composite material which has a low thermal conductivity and a high mechanical strength, and is also free of organic propellants.

This is solved by a composite material that contains 5-97 vol% aerogel particles and at least one adhesive, and is characterized in that the diameter of the aerogel particles is less than 0.5 mm.

The adhesive(s) form(s) a matrix which binds or surrounds the aerogel particles and passes through the entire composite material as a continuous phase.

With a content of aerogel particles that is significantly below 5 vol% in the composition, the positive properties of the aerogel particles would be largely lost due to their low concentration. Such a composition would no longer have low densities and thermal conductivities.

A content of aerogel particle that is significantly greater than 97 vol% would lead to a content of adhesive below 3 vol%. In this case, the content would be too low to guarantee

sufficient binding of the aerogel particles to one another, mechanical pressure resistance and bending strength.

The content of aerogel particles preferably lies in the range from 10-97 vol%, particularly preferably in the range from 20-95 vol%, and more particularly in the range from 40-95 vol%.

According to the invention, the diameter of the aerogel particles is less than 0.5 mm, preferably smaller than 0.2 mm. For electronic applications, they can be considerably smaller, but preferably greater than 1 μm . The particle diameter refers to the average diameter of the individual aerogel particle, since the aerogel particle need not necessarily have a spherical shape for production reasons, for instance, because of grinding.

The use of small aerogel particles leads to a more homogeneous distribution in the composition, which causes the composite material to exhibit a nearly uniform low thermal conductivity and dielectric constant at all points, particularly on the surfaces as well.

Small aerogel particles also lead to improved mechanical stability against the formation of ruptures and cracks for the same aerogel content, because such large strains cannot build up locally under stress.

A particularly high content of aerogel particles in the composite material can be achieved by employing a bimodal distribution of the particle sizes.

Suitable aerogels for the compositions according to the invention are those based on metal oxides which are suited for the sol-gel technique (C.J. Brinker, G.W. Scherer, Sol-Gel Science, 1990, Chapters 2 and 3), such as Si or Al compounds, or those based on organic substances which are suited for the sol-gel technique, such as melamine formaldehyde condensates (US-A 5 086 085) or resorcinol formaldehyde condensates (US-A-4 873 218). They can also be based on mixtures of the aforementioned materials. Aerogels containing Si compounds, are preferably used particularly SiO_2 aerogels and more preferably SiO_2 xerogels. To reduce the radiation component of the thermal conductivity, the aerogel may contain IR opacifiers such as carbon black, titanium dioxide, iron oxide or zirconium oxide, as well as mixtures of the above.

In a preferred embodiment, the aerogel particles have permanently hydrophobic surface groups. Suitable groups for permanent hydrophobization are, for instance, silyl groups with the general formula $-\text{Si}(\text{R})_n$, where $n = 1, 2$ or 3 , preferably trisubstituted silyl groups, where the residues generally are each independently, identically or differently a hydrogen atom or a nonreactive, organic, linear, branched, cyclic, aromatic or heteroaromatic residue, preferably a C_1 - C_{18} alkyl or C_6 - C_{14} aryl, particularly preferably a C_1 - C_6 alkyl, cyclohexyl or phenyl, particularly methyl or ethyl. Particularly advantageous for the permanent hydrophobization of the aerogel is the use of trimethylsilyl groups. The insertion of these can be done as described in WO 94/25149, or by gas-phase reaction between the aerogel and, for instance, an activated

trialkylsilane derivative, such as chlorotrialkylsilane or hexaalkyldisilazane (compare R. Iler, *The Chemistry of Silica*, Wiley & Sons, 1979). Compared with OH groups, the thus-manufactured hydrophobic surface groups further reduce the dielectric loss factor and the dielectric constant. Aerogel particles with hydrophilic surface groups can adsorb water, depending on the humidity, which cause the dielectric constant and the dielectric loss factor to vary with the humidity. This is often not desired for electronic applications. The use of aerogel particles with hydrophobic surface groups prevents this variation, since no water is adsorbed. The selection of the residues is also guided by the typical temperature of use.

If aerogel particles with hydrophobic surface groups are used, one obtains a hydrophobic composite material when using very small particle diameters, since the hydrophobic aerogel present is distributed homogeneously and very finely. In principle, however, all aerogels are suitable.

Beyond that, it is true that the thermal conductivity of aerogels decreases with increasing porosity and decreasing density. Therefore, aerogels with porosities over 60% and densities under 0.6 g/cm^3 are preferred. Particularly preferred are aerogels with densities below 0.4 g/cm^3 .

In principle, all known adhesives are suited for manufacturing the composite materials according to the invention, an adhesive being understood in the present application as a nonaqueous binder. Nonaqueous binders in the sense of the present application are solutions or solution mixtures that contain less than 50 wt% water. The adhesive is employed in liquid form, i.e. as a fluid, melt, solution dispersion or suspension, or as a solid powder.

Both physically setting and chemically curing monocomponent adhesives, as well as chemically curing bicomponent adhesives, can be used.

Suitable physically setting monocomponent adhesives are, for instance, melt adhesives, such as ethylene vinyl acetate copolymers and polyamides, polyethylene waxes, dispersion adhesives, solvent adhesives and plastisols.

Suitable chemically curing monocomponent adhesives are, for instance, thermosetting epoxy resins, formaldehyde condensates, polyimides, polybenzamidazoles, cyanacrylates, polyvinyl alcohols, polyvinyl butyrals, anaerobic adhesives, moisture-curing silicones, as well as light- and UV-curing systems, with polyvinyl butyrals and/or polyvinyl alcohols or phenol, resorcinol, urea and melamine formaldehyde resins as well as mixtures of these being preferred.

Suitable chemically curing bicomponent adhesives are, for instance, methacrylates, bicomponent silicones, cold-curing epoxy resins and cold-curing polyurethanes.

The production and application of phenol, resorcinol, urea and melamine formaldehyde resins is known and described in, for instance, *Plastics Handbook 10 "Thermosetting Materials,"* ed. Prof. Woebcken, 2nd ed. 1988, Hanser Verlag.

The adhesive is generally employed in an amount of from 3-95 vol% of the composite material, preferably in an amount of 3-90 vol%, particularly preferably in an amount of 5-80 vol%, and specifically in an amount from 5-60 vol%. The selection of the binder is done according to the desired mechanical and thermal properties of the composite material.

In the selection of the adhesives, moreover, those products are selected which essentially do not penetrate into the interior of the porous aerogel particles. The penetration of the adhesive into the interior of the aerogel particles can be influenced by the control of the temperature, as well as by the selection of the adhesive.

To reduce the radiation component of the thermal conductivity, the composite material can contain IR opacifiers, such as carbon black, titanium oxide, iron oxides or zirconium oxide or mixtures of the above, which is particularly advantageous for application at high temperatures.

Moreover, the composite material may contain up to 85 vol% fillers, such as sawdust, asbestos and preferably cellulose in order, for instance, to improve the mechanical properties. The content of fillers with respect to the composite material is preferably less than 70% and particularly preferably in the range from 0-50 vol%.

The composite material can, furthermore, also contain at least one fiber material. The addition of fibers is advantageous, in particular, for thermal applications and in regard to crack formation and rupture strength.

Compared to a material that consists only of aerogel particles, which are connected via their surfaces or embedded in a plastic matrix, even a slight volume content of fiber materials surprisingly leads to a considerable mechanical improvement with the same content by volume of adhesive, since they take over essential components of the load. If a higher fiber content by volume is used and only a small amount of adhesive, then a porous material can be obtained in which the fibers bound together by the adhesive form a mechanically stable framework into which the aerogel particles are embedded. The air pores that then appear bring about a higher porosity and thus an improved sound dissipation.

As the fiber material, it is possible to use natural fibers, such as cellulose, cotton or flax fibers, as well as artificial fibers, where both inorganic fibers, such as glass fibers, mineral fibers, silicon carbide fibers or carbon fibers, and organic fibers, such as polyester fibers, polyamide fibers, or polyaramide fibers can be employed. These fibers can be new or produced from wastes such as shredded glass fiber wastes or rag residues. The fibers can also be coated, such as polyester fibers that are metallized with a metal such as aluminum.

The fibers may be flat or curled as individual fibers, as padding, or as nonwoven or woven fiber fabric. Nonwoven and/or woven fiber fabrics can be contained in the composite material in coherent form or in the form of several small pieces.

The fibers can have round, trilobal, pentalobal, octalobal, ribbon, Christmas tree, dumbbell or other star-shaped profiles. Hollow fibers can likewise be used.

In general, fibers with a diameter between 0.1 μm and 5 mm are used. For a set content by volume of fibers, the use of smaller diameters typically leads to more fracture-resistant composite materials.

The diameter of the fibers contained in the composite material should preferably be smaller than the average diameter of the aerogel particles, in order to be able to bind a large content of aerogel in the composite material. By selecting very thin fibers, the composite material becomes more easily flexible.

The length of the fibers is not restricted in any way. Preferably, however, the length of the fibers should be greater than the average diameter of the aerogel particles.

The mechanical strength of the composite material can be influenced by the length and distribution of fibers in the composite material. For this application purpose, fibers whose length is between 0.5-10 cm are therefore preferably used.

Furthermore, mixtures of the above-mentioned types can be used.

The stability and the thermal conductivity of the composite material increase with increasing fiber content. In order to avoid a significant elevation of the thermal conductivity due to the added fibers, the content of fibers by volume should preferably lie from 0.1-40 vol%, particularly preferably in the range from 0.1-15%.

The thermal conductivity of the fiber material should also preferably be $< 1 \text{ W/m}\cdot\text{K}$.

By a suitable choice of fiber diameter and/or material, the radiation component of the thermal conductivity can be reduced and a greater mechanical strength can be obtained.

For this purpose, the fiber diameter should be

- a) preferably 0.1-30 μm for nonmetallized fibers and/or for
- b) metallized fibers, 0.1-20 μm .

The radiation component of the thermal conductivity can be further reduced by using blackened fibers, such as polyester fibers blackened with carbon black, or carbon fibers directly.

For better binding to the matrix, the fibers can be coated with sizings or coupling agents as is usual for glass fibers, for instance.

Either the fibers and the aerogels are connected and held together by the adhesive, or the adhesive serves as a matrix material in which the fibers and the aerogel particles are embedded.

In addition, lubricants such as zinc stearate, pigments such as titanium dioxide, plasticizers such as glycerin and o,p-toluenesulfonamide and/or acidic or acid-hydrolyzing curing accelerators can be contained in small amounts in the composite material.

If the composite material should be hydrophilic because of the adhesive used and/or because of hydrophilic aerogel particles, then a subsequent treatment can be done, if desired,

which gives hydrophobic properties to the composite material. Suited for this purpose are all materials known to the person skilled in the art which provide the composite material with a hydrophobic surface, such as lacquers, films, silylation agents, silicone resins, and inorganic and/or organic binders.

Furthermore, so-called "coupling agents" can be employed in the adhering process. They produce a better contact of the adhesive with the surface of the aerogel particles and can additionally enter into a firm bond with both the aerogel particles and the adhesive.

The molded articles produced according to the invention from aerogel granules, particularly in mat form, containing the composite material according to the invention, or consisting essentially of it, preferably have a density of less than 0.6 g/cm^3 and preferably a thermal conductivity of less than $100 \text{ mW/m}\cdot\text{K}$. Particularly preferably, the thermal conductivity is less than $50 \text{ mW/m}\cdot\text{K}$ and is specifically in the range of $20\text{-}40 \text{ mW/m}\cdot\text{K}$.

The fire classification of the composite material obtained after drying is determined by the fire classification of the aerogel and the adhesive as well as possibly that of the fiber material. In order to obtain as favorable a fire classification of the composite material as possible (low-flammable to noncombustible), adhesives are used which are of low flammability, such as urea formaldehyde and melamine formaldehyde resins, silicone resin adhesives, polyimide and polybenzimidazol resins, as well as fibers of noncombustible material, such as mineral, glass or SiC fibers.

To produce the composite materials according to the invention, the aerogel particles are bonded together by means of at least one adhesive. The bonding of the individual particles to one another can be done here point-by-point as it were. Such a surface coating can be achieved, for instance, by spraying the aerogel particles with the adhesive. The coated particles are then, for instance, filled into a form and cured in the form.

In a preferred embodiment, the spacing between the individual particles is then completely or partially filled with adhesive. Such a composition can be achieved, for instance, by mixing the aerogel particles, 0 and optionally the fibers, with the adhesive.

The mixing can be performed here in any conceivable manner. Thus, it is possible, on the one hand, to introduce the two or more components simultaneously into the mixing device; on the other hand, one of the components can be presented and the other(s) then added.

The mixing device necessary for the mixing process is also not restricted in the least. Any mixing device familiar to the typical person skilled in the art can be used for this purpose.

The mixing process is conducted until there exists an approximately uniform distribution of the aerogel particles in the compound. The mixing process can be controlled both via the duration and the speed of the mixing device.

Then the forming and curing of the mixture in the mold occurs, taking place, depending on the type of adhesive, by heating and/or evaporation of the solvent and/or dispersant used, or in case melt adhesives are used, by cooling to below the melting temperature of the adhesive.

In a preferred embodiment, the mixture is compression-molded. It is possible here for the typical person skilled in the art to select the appropriate mold and the appropriate compression tools. Due to the high air content of the aerogel-containing molding compositions, the use of vacuum compression is advantageous. In a preferred embodiment, the aerogel-containing molding compositions are compression-molded into mats. In order to prevent sticking of the molding composition to the compression-mold, the aerogel-containing mixture to be compression-molded can be separated from the compression mold by separating paper. The mechanical strength of the aerogel-containing mats can be improved by laminating wire gauzes, nonwoven fabrics or papers onto the mat surface. The wire gauzes, nonwoven fabrics or papers can be applied subsequently to the aerogel-containing mats, wherein the wire gauzes, nonwoven fabrics or papers can be first impregnated with melamine resins, for instance, and then bonded under pressure in a heatable mold to the mat surfaces, as well as, in a preferred embodiment, in a single work step by inserting the wire gauzes, nonwoven fabrics or papers, optionally first impregnated with melamine resins, into the compression mold, placing the aerogel-containing molding composition to be compression-molded on top of them and subsequently press-compacting them under pressure and temperature into an aerogel-containing composite mat.

Depending on the adhesive employed, the compression molding is generally done at compacting pressures of 1-1000 bar and temperatures of 0-300°C. In the case of the preferred phenol, resorcinol, urea and melamine formaldehyde resins, the compression-molding generally takes place in arbitrary molds at pressures of 5-50 bar, particularly preferably 10-20 bar, and temperatures preferably of 100-200°C, particularly preferably, 130-190°C and specifically between 150-175°C.

After curing, the composite materials according to the invention are suitable thermal insulation materials because of their low thermal conductivity.

The invention is described in more detail below on the basis of embodiments, without, however, being limited thereto.

The hydrophobic aerogels were produced analogously to the process disclosed in DE-A-43 42 548.

The thermal conductivities of the aerogel granules were measured with the heating wire method (see, for instance, O. Nielsson, G. Rüschenpöhler, J. Groß, J. Fricke, High Temperatures--High Pressures, Vol. 21 (1989), 267-274).

The thermal conductivities of the molded articles were determined according to DIN 52612.

Example 1

Molded article of aerogel and melamine formaldehyde resin

20 g of hydrophobic aerogel (94 vol%) and 5 g Madurit® MW 909 melamine formaldehyde powdered resin (6 vol%) are thoroughly mixed. The hydrophobic aerogel granules have a grain size in the range of 50-250 μm , a powder density of 0.1 g/cm^3 , a BET surface of 570 m^2/g and a thermal conductivity of 15.7 $\text{mW}/\text{m}\cdot\text{K}$. The bottom of the compression mold with a surface of 12 x 12 cm is covered with separating paper. The aerogel-containing molding composition is evenly distributed on top of it and the entirety is covered with a separating paper. It is pressed at a temperature of 170°C and a pressure of 10 bar for 30 min. The obtained molded article has a density of 0.32 g/cm^3 and a thermal conductivity of 30 $\text{mW}/\text{m}\cdot\text{K}$.

Example 2

Molded article of aerogel and melamine formaldehyde resin and lubricant

20 g of hydrophobic aerogel (93 vol%), 5 g Madurit® MW 909 melamine formaldehyde powdered resin (6 vol%) and 1 g of zinc stearate (1 vol%) are thoroughly mixed and compressed in a mold with a bottom surface of 12 x 12 cm at a temperature of 170°C and a pressure of 10 bar for 30 min. The hydrophobic aerogel granules have a grain size in the range of 50-250 μm , a powder density of 0.117 g/cm^3 , a BET surface of 540 m^2/g and a thermal conductivity of 18.4 $\text{mW}/\text{m}\cdot\text{K}$. The obtained molded article has a density of 0.33 g/cm^3 and a thermal conductivity of 33 $\text{mW}/\text{m}\cdot\text{K}$.

Example 3

Molded article of aerogel, melamine formaldehyde resin and filler

140 g of hydrophobic aerogel granule from Example 2 (77 vol%), 75 g Madurit® MW 909 melamine formaldehyde powdered resin (10 vol%) and 17.5 g of type 402-2B microcellulose from the Mikrotechnik firm of Miltenberg am Main (13 vol%) are thoroughly mixed. The bottom of the compression mold with a surface of 30 x 30 cm is covered with separating paper, followed by a wire gauze with a mesh size of 5 mm. The aerogel-containing molding composition is uniformly spread on top of that, covered with a wire gauze of 5 mm mesh size, and the entirety is covered with a separating paper. It is compressed at a temperature of 160°C and a pressure of 20 bar for 9 min with subsequent cooling. The molded article obtained as a stable mat has a density of 0.38 g/cm^3 and a thermal conductivity of 37 $\text{mW}/\text{m}\cdot\text{K}$.

Example 4

Molded article of aerogel, melamine formaldehyde resin and various fiber materials and/or filler
 140 g of a hydrophobic SiO_2 aerogel from Example 2, 75 g Madurit® MW 909 melamine formaldehyde powdered resin and the fiber materials and/or fillers listed in Table 1 are thoroughly mixed and pressed at a temperature of 160°C and a pressure of 10-20 bar for 10 min in a mold with a bottom surface of 30 x 30 cm. The densities of the mats obtained are listed in Table 1.

Table 1. Composition of the molding compositions in vol% and densities of the molded articles obtained

Nr. ①	Aerogel [Vol.-%]	Madurit MW 909 [Vol.-%]	Fasermaterial ② [Vol.-%]	Füllstoff ③ [Vol.-%]	Dichte ④ [g/cm ³]
A	77 %	10 %	Steinwolle 13 % ⑤		0,31
B	77 %	10 %	Textilfasern 13 % ⑥		0,36
C	77 %	10 %	Glasfasern 13 % ⑦		0,38
D	83 %	11 %		⑧ Mikrocellulose 6 %	0,39
E	88 %	11 %	Glasfaser 1 % ⑦		0,36
F	78 %	11 %	Steinwolle 11 % ⑤		0,33
G	78 %	11 %		⑧ Mikrocellulose 11 %	0,32
H	77 %	10,5 %	Glasfaser 0,5 % ⑦	⑧ Mikrocellulose 12 % ⑧	0,32
I	77 %	10,7 %	Glasfaser 0,3 % ⑦	⑧ Mikrocellulose 12 % ⑧	0,40

- Key: 1 No.
 2 Fiber material (vol%)
 3 Filler (vol%)
 4 Density (g/cm³)
 5 Rock wool
 6 Textile fibers
 7 Glass fibers
 8 Microcellulose

Comparative example

Molded article of melamine formaldehyde resin and silicic acid

90 g of Madurit® MW 396 melamine formaldehyde powdered resin are thoroughly mixed with 100 g Perkasil® KSD 404 silicic acid, 30 g microcellulose and 2.5 g zinc stearate, and compressed for 4 min in a mold with a bottom surface of 12 x 12 cm at a temperature of 155°C and a pressure of 270 bar. The obtained molded article has a density of 1.37 g/cm³ and a thermal conductivity of 150 mW/m·K.

Example 5

Molded article of aerogel and polyvinyl alcohol

90 wt% hydrophobic aerogel granules and 10 wt% polyvinyl alcohol solution are thoroughly mixed. The hydrophobic aerogel granules have a grain size of less than 500 µm, a powder density of 75 kg/m³, a BET surface of 610 m²/g and a thermal conductivity of 15 mW/(m·K). The polyvinyl alcohol solution consists of 10 wt% Mowiol® type 40-88 and 90 wt% ethanol.

The bottom of the compression mold with a surface of 12 x 12 cm is covered with separating paper. The aerogel-containing molding composition is uniformly distributed on top of it and the entirety is covered with separating paper. It is compressed at ambient temperatures with a pressure of 70 bar for 2 min and subsequently dried.

The obtained molded article has a thermal conductivity of 24 mW/(m·K).

Example 6

Molded article of aerogel and polyethylene wax

60 wt% hydrophobic aerogel granules from Example 5 and 40 wt% Ceridust® 130 polyethylene wax powder are thoroughly mixed.

The bottom of the compression mold with a surface of 12 x 12 cm is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with separating paper. It is compressed at 170°C and a pressure of 70 bar for 30 min.

The obtained molded article has a thermal conductivity of 25 mW/(m·K).

Example 7

Molded article of aerogel and polyethylene wax

50 wt% hydrophobic aerogel granules from Example 5 and 50 wt% Hoechst-Wax PE 520 polyethylene wax are thoroughly mixed.

The bottom of the compression mold with a surface of 12 x 12 cm is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and

the entirety is covered with separating paper. It is compressed at 180°C and a pressure of 70 bar for 30 min.

The obtained molded article has a thermal conductivity of 28 mW/(m·K).

Example 8

Molded article of aerogel and polyvinyl butyral

80 vol% hydrophobic aerogel granules and 20 vol% Mowital® polyvinyl butyral powder (Polymer F) are thoroughly mixed. The hydrophobic aerogel granules have a grain size of less than 500 µm, a powder density of 75 kg/m³, a BET surface of 640 m²/g and a thermal conductivity of 11 mW/(m·K).

The bottom of the compression mold with a surface of 30 x 30 cm is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with a separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 361 kg/m³ and a thermal conductivity of 33 mW/(m·K).

Example 9

Molded article of aerogel and polyvinyl butyral

90 vol% hydrophobic aerogel granules from Example 8 and 10 vol% Mowital® polyvinyl butyral powder (Polymer F) are thoroughly mixed.

The bottom of the compression mold with a surface of 30 x 30 cm is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with a separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 335 kg/m³ and a thermal conductivity of 24 mW/(m·K).

Example 10

Molded article of aerogel and polyvinyl butyral

95 vol% hydrophobic aerogel granules from Example 8 and 5 vol% Mowital® polyvinyl butyral powder (Polymer F) are thoroughly mixed.

The bottom of the compression mold with a surface of 30 x 30 cm is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 246 kg/m^3 and a thermal conductivity of $19 \text{ mW/(m}\cdot\text{K)}$.

Example 11

Molded article of aerogel, polyvinyl butyral and fibers

90 vol% hydrophobic aerogel granules from Example 8, 8 vol% Mowital® polyvinyl butyral powder (Polymer F) and 2 vol% Trevira® high-strength fibers are thoroughly mixed.

The bottom of the compression mold with a surface of $30 \times 30 \text{ cm}$ is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 269 kg/m^3 and a thermal conductivity of $20 \text{ mW/(m}\cdot\text{K)}$.

Example 12

Molded article of aerogel, polyvinyl butyral and recycled fibers

80 vol% hydrophobic aerogel granules from Example 8, 10 vol% Mowital® polyvinyl butyral powder (Polymer F) and 10 vol% coarsely chopped-up polyester fibers from recycled fibers are thoroughly mixed.

The bottom of the compression mold with a surface of $30 \times 30 \text{ cm}$ is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 282 kg/m^3 and a thermal conductivity of $25 \text{ mW/(m}\cdot\text{K)}$.

Example 13

Molded article of aerogel, polyvinyl butyral and film residues

80 vol% hydrophobic aerogel granules from Example 8, 10 vol% Mowital® polyvinyl butyral powder (Polymer F) and 10 vol% polyester film snips with a thickness of $14 \mu\text{m}$ are thoroughly mixed.

The bottom of the compression mold with a surface of $30 \times 30 \text{ cm}$ is covered with separating paper. A molding composition containing aerogel is uniformly distributed over it and the entirety is covered with separating paper. It is compressed at 220°C for 30 min to a thickness of 18 mm.

The obtained molded article has a density of 355 kg/m^3 and a thermal conductivity of $26 \text{ mW/(m}\cdot\text{K)}$.

Claims

1. Composite material that contains 5-97 vol% aerogel particles and at least one adhesive, characterized in that the diameter of the aerogel particles is less than 0.5 mm.
2. Composite material according to Claim 1, characterized in that the content of aerogel particles lies in the range of 20-95 vol%.
3. Composite material according to Claim 1 or 2, characterized in that the diameter of the aerogel particles is less than 0.2 mm.
4. Composite material according to at least one of Claims 1-3, characterized in that the grain sizes of the aerogel particles have a bimodal distribution.
5. Composite material according to at least one of Claims 1-4, characterized in that the aerogel is an SiO_2 aerogel.
6. Composite material according to at least one of Claims 1-5, characterized in that the aerogel particles have permanently hydrophobic surface groups.
7. Composite material according to at least one of Claims 1-6, characterized in that the aerogel particles have porosities over 60% and densities under 0.6 g/cm^3 .
8. Composite material according to at least one of Claims 1-7, characterized in that the aerogel particles and/or the composite material contain at least one IR opacifier.
9. Composite material according to at least one of Claims 1-8, characterized in that the composite material contains fibers.
10. Composite material according to Claim 9, characterized in that the content of the fibers lies in the range of 0.1-40 vol%.
11. Composite material according to at least one of Claims 1-10, characterized in that the composite material contains fillers.
12. Composite material according to at least one of Claims 1-11, characterized in that phenol, resorcinol, urea and melamine formaldehyde resins, as well as mixtures of the above, are used as the adhesive.
13. Composite material according to at least one of Claims 1-11, characterized in that polyvinyl butyrals and/or polyvinyl alcohols are used as the adhesive.
14. Composite material according to at least one of Claims 1-13, characterized in that it has a density below 0.6 g/cm^3 and a thermal conductivity of less than $100 \text{ mW/(m}\cdot\text{K)}$.
15. Composite material according to at least one of Claims 1-14, characterized in that the composite material has at least one hydrophobic surface.

16. Method of manufacturing a composite material according to at least one of Claims 1-15, characterized in that the aerogel particles are mixed with adhesive and the mixture is subjected to forming and curing.
17. Method according to Claim 16, characterized in that the mixture is compression molded for forming and/or curing.
18. Method according to Claim 17, characterized in that the compression molding is performed at compression pressures of 1-1000 bar and temperatures of 0-300°C.
19. Use of a composite material according to at least one of Claims 1-15 as a thermal insulator.
20. Molded article containing a composite material according to at least one of Claims 1-15.
21. Molded article consisting essentially of a composite material according to at least one of Claims 1-15.
22. Molded article according to Claim 20 or 21, characterized in that it is the form of a mat.

INTERNATIONAL SEARCH REPORT

Int ional Application No

PCT/EP 96/03867

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B14/06 C04B30/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 672 635 A (BASF AG) 20 September 1995 see page 3, line 4 - line 47 see column 4, line 3 - line 29; claims ---	1-3,5-8, 12, 14-16, 19-22
P,X	DE 44 37 424 A (HOECHST AG) 25 April 1996 see page 3, line 7 - page 6, line 49 ---	1-10,15, 19-22
A	DE 29 41 606 A (GRÜNZWEIG + HARTMANN UND GLASFASER AG) 23 April 1981 see page 7, line 37 - page 8, line 5 see page 9, line 8 - page 10, line 38 ---	1,5,8,9, 12,16, 17,19-22
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Theodoridou, E

INTERNATIONAL SEARCH REPORT

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P,A

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/EP 96/03867

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